METHOD AND INSTALLATION FOR CARRYING OUT GLOW DISCHARGE PROCESSES

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The present invention relates to a method of and apparatus for performing metallurgical, chemical, or other technical processes under the influence of an electric glow discharge in a discharge vessel containing electrodes which carry an electric potential, and insulated leads for applying the potentials to the said electrodes. In such glow discharge vessels the greatest concentration of energy is known to be located principally in the vicinity of the electrode which carries the negative potential, even if the latter acts only temporarily as a cathode as would be the case when the discharge vessel is operated by alternating current. Consequently such glow discharge phenomena are exceptionally useful for treating the surface of materials which operate as a cathode because the high concentration of energy is then localised directly on the treated metal surface.

However, for the performance of processes which are not intended to take place on a metal surface, such as chemical reactions between gaseous media, the localisation of the exceptionally effective discharge phenomena on the cathodic electrode is undesirable. On the one hand, it is difficult to arrange that the entire volume of reacting gaseous media will pass through the glow discharge zone which develops on the cathode surface and, on the other hand, the presence of a metallic surface in the immediate vicinity of the reaction zone is often a drawback because of the tendency of the metal to participate in the reaction. To overcome these difficulties a proposal has already been made to enclose the metallic cathode in a chemically neutral material. However, the electric resistance of such materials is generally very high and therefore causes the energy density to fall to very low values.

The present invention seeks to solve this problem by relieving at least one of the electrodes participating in the maintenance of the discharge of at least part of the load due to the energy of discharge in favour of part of the gas space surrounding the electrode and to this end, on the one hand, creates a pressure gradient in the zone around the electrode in which the gas pressure diminishes with increasing distance from the electrode and, on the other hand, suitably locates the cooperating electrodes to favour a migration of the discharge away from the electrode and into the zone of decreasing pressure.

The apparatus for performing this method comprises a discharge space enclosed in an envelope and at least one nozzle which projects into said space and which is adapted to project a jet into the space through which the glow discharge passes.

The invention will be hereinafter described with reference to an illustrative embodiment of apparatus for performing the method shown in the accompanying drawing.

The discharge gap 1 is completely enclosed within a metal envelope 2 which may be jacketed for the purpose of permitting a coolant to be conducted in the direction indicated by arrow 3 through the space 4 between the envelope and the outside wall of the jacket. The top of the chamber 1 has an airtight cover 5 consisting of an electrically insulating material and containing a metal admission element 6 with a duct 7 which terminates inside the furnace chamber 1 in the shape of a nozzle 8. The wall which encloses the duct 7 and the nozzle 8 is provided with channels 9 and 10 for conveying a coolant such as water or liquid air, which enters in direction 11 and, after flowing round the nozzle 8, leaves in direction 12. The joint between metal and insulating material in the cover plate 5 is protected in a well known manner by the provision of clearances 13 and 14 respectively.

Since the intention is at least partly to reduce the energy of glow discharge affecting the nozzle and that part of the admission element 6 which projects into the discharge chamber 1, whenever the admission element functions as cathode, a ring 15a which acts as a cooperating electrode is arranged in close proximity to and opposite the nozzle orifice, the said ring being supported by part of the lead-in 16a which passes into the chamber through an insulated bushing 17a. The internal diameter of ring 15a should be as small as possible but in no circumstances should it impede a gas jet issuing from the nozzle orifice. Ring 15a is connected through a switch 16c with the positive terminal of a source of electric potential 18, of which the negative terminal is connected with the induction element 6 through a switch 16. On the other hand, switch 16a is connected with a source of potential 19, for the supply for instance of an alternating potential, which has a centre tapping joined to a lead-in 17, for a ring 15b, whereas the other pole is connected via a third switch 16c and lead-in 17c with a ring 15c.

Through a pipe 21 controlled by valve means 20 the substance it is intended to process, such as for instance an atomised liquid, possibly suspended in a carrier gas, is supplied to the induction element 6. To this end a fine dispersion of the liquid discharged from a hopper 25 is produced in a mixer 22 by a high-pressure current of gas which reaches an atomiser 24 through a pipe 23, and the mist created by the finely dispersed liquid sus- pended in the carrier gas is then conveyed through pipe 21 to the nozzle 8 as soon as valve 20 has been opened. The pressure P1 can be read on a pressure gauge 26. At the bottom end of the furnace chamber 1 is a suction pipe 27 connected through a stop valve 28 to a pumping set 29. This is designed to create in the furnace chamber 1 at the junction of the suction pipe 27 a desired pressure P3 which can be read on a pressure gauge 34, and to maintain this pressure even where a gas stream is injected through nozzle 8 at a pressure P1. The pressure ratio P1/P3 may be raised to high values.

For the purpose of starting-up, the valves 20 and 24 can be closed and an auxiliary gas induced into the furnace chamber 1 through pipe 30 and valve 31, a pump 33 connected through a valve 32 with pipe 27 being at the same time arranged to evacuate the furnace chamber to a desired low level of pressure.

The final product of the glow discharge process is removed from the furnace chamber 1 through a suitable gating device 35 which is not relevant to the invention and therefore need not be described.

For establishing stationary operating conditions, the suction head of pump 29 and the volume of gas induced through nozzle 8 are related to the desired pressure ratio and the mini- mum pressure ratio P1/P3 for instance between 1:00:1 and 10:1 is established. In the neighbourhood of the nozzle orifice and within a spatial zone which symmetrically surrounds the axis of the gas jet, for instance in the zone indicated by the dotted line 36, the pressure will then exceed the pressure P2. A difference in the pressure gradient P—P3 smaller than the gradient P1—P2 will then arise at every point within the said zone. According to the aerodynamic conditions produced by the gas
jet which issues from the nozzle 8 the shape of the jet and that of the associated isobars as well as the pressure gradient will vary, but in any case the pressure in the jet will decrease with increasing distance from the orifice of nozzle 8.

Such a zone of decreasing pressure adjoining the nozzle 8 which in this example is assumed to act as the cathode and the orifice of the ring-shaped anode 15a in a displacement of the high-energy glow discharge away from the orifice of the nozzle 8 towards the ring-shaped anode 15a. This result not only relieves the nozzle 8 of the load but the energy of discharge that becomes available within the zone of decreasing pressure or in parts of said zone will at the same time permit chemical reactions to be performed in the gas jet without adversely affecting the neighbouring metal electrodes. A particularly useful feature is that the comparatively high velocity of the jet reduces the dwell of the reacting reagents in the high-energy zone of the glow discharge and that the reaction products are rapidly carried out of the reaction zone.

The high energy load on nozzle 8 will already be relieved if, apart from the nozzle 8 of the induction element, potential is applied only to ring 15a to enable it to act as an anode, that is to say if only the two switches 16 and 16c are closed and the switches 16b and 16c remain open. Of course, the ring 15a may be replaced by an electrode of some other shape that is symmetrical in relation to the jet axis, for instance by a cylindrical electrode. Moreover, the source of potential 18 need not be a direct current potential supply. An intermittent or pulsed direct current potential or a low or high-frequency alternating potential may likewise be used. An alternative method of operation would be for the nozzle 8 and the inducting element 6 to serve as a permanent anode in cooperation with electrode 15a as the cathode, because the vicinity of the cathode will then still be a zone of decreasing pressure and a tendency for the glow discharge to shift away from the cathode into this zone will again be observed.

When the two switches 16b and 16c are closed the employment of the additional source of direct current or alternating current potential 19 of the electrodes 15b and 15c will have the effect of still further increasing the tendency of the discharge to detach itself from nozzle 8 and to move in the direction of the issuing jet. It is by no means essential to the performance of the present method that the nozzle 8 or the induction element should always actively participate in the creation of the discharge by acting as one of the electrodes. For instance, if switch 16 is opened and only the three switches 16a, 16b and 16c are closed and assuming the source 19 to supply a direct current potential, then the ring electrodes 15b and 15c may act as the cathode and the two ring electrodes 15b and 15c as two anodes. The gas jet will still create a zone of decreasing pressure in the neighbourhood of this new cathode 15c and thereby induce the high-energy glow discharge to detach itself from the cathode ring 15a and to migrate into the space between the two electrodes 15b and 15c. A similar effect can be achieved by using a source 19 which supplies an intermittent or pulsed direct current or a low or high-frequency alternating current potential.

The counter-electrodes 15a, 15b, 15c diagrammatically shown in the drawing may, of course, have some alternative shape, provided that when they cooperate with the relative cathode they will favour the migration of the high-energy glow discharge from the said cathode into the zone of decreasing pressure. Moreover, the counter-electrodes 15b and 15c could be dispensed with and the lower part of the discharge chamber 1 filled with a material it was desired to treat metallurgically, the said material being at a potential differing from that of nozzle 8 and the gas jet impinging upon the material. Nor is it absolutely essential that the direction of the jet issuing from the nozzle 8 should coincide with the lines of force of the electric field between the electrodes which maintain the discharge, from the fact that the gas jet might be arranged to be at an angle or even normal thereto. Moreover, several inducting elements could be provided, each acting as cathodes and each cooperating with its associated or with a common anode. Also the provision of several nozzles that do not participate in the discharge may in special cases be a useful arrangement.

The method that has been described can be especially easily performed if P2 is maintained between 1 and 10 mm. mercury, because gaseous substances that are to be processed may then be induced through nozzles of 1 sq. mm. internal cross section. These will then create a readily reproducible reaction zone, for instance 200 mm. in length, and of 10 mm. maximum width. The reaction vessel may be relatively compact and consist, for instance, of an iron vessel 60 cms. across and 100 cms. in height, and the dissipation of the generated heat will offer no special difficulty. To maintain a vacuum pressure of something like 5 to 10 mm. Hg the stated internal nozzle sections would require the provision of a pumping set capable of discharging 75 cub. metres per hour. However, the quantitative throughput would then be of the order of something like 12 litres per minute.

In a plant intended for industrial applications it is principally the throughput that matters, so that greater nozzle sections or the provision of several nozzles working in parallel would be required, especially when dealing with substances in powder form. However, it will be readily understood that at the pressures which have been mentioned and which call for a pumping capacity equal to something like a hundred times the volume of gas (related to standard conditions) induced through the nozzle during the reference period, the necessary machinery would rapidly assume proportions which could not be accepted in economical working conditions.

A careful study of the problem involved has, however, shown a way of satisfactorily overcoming this difficulty and of making the method amenable to industrial application. As has been described, the performance of the method requires the creation of an homogeneous pressure distribution inside the reaction chamber, comprising a zone adjacent the nozzle orifice with a steep pressure gradient from the higher pressure immediately at the nozzle orifice to the lower pressure in the more remote interior. This zone represents the space in which the reaction takes place and in which the processed substances dwell for a certain period of time which depends upon their velocity. However, it has been found that the ratio between maximum and minimum pressure within this reaction zone is not as important as the concentration of the major portion of the available pressure gradient within this zone. Consequently, when increasing the effective nozzle sections the pressure in the interior may at the same time be raised, conveniently to over 20 mm. Hg or even above 50 mm. Hg. If necessary, the pressure at which the substances for processing are forced through the nozzles may then likewise be raised. By reducing the vacuum to between 20 and 50 mm. Hg or even more, the delivery of the pump can be appreciably raised and a much higher throughput assured.

The present method permits the performance of glow discharge processes between reagents in gas or vapour form, but it may as well be applied to liquid or solid substances that are finely dispersed in a carrier gas, provided suitable nozzles are employed for the purpose. Attention may also be drawn to the fact that the injection of gas-forming liquid or solid particles may sensibly affect the shape of the decreasing pressure zone by the presence of the volume of gas that is formed.

As has been mentioned, the location of the electrodes must be determined in a suitable way to favour the dis-
placement of the discharge away from the cathode into part of the decreasing pressure zone. If a metallic nozzle is used to serve as a negative electrode, then care must be taken to see that at least at the orifice of the nozzle a glow discharge is actually formed, which is capable of being displaced in the direction of the issuing jet. The migration of the discharge zone is also assisted by raising the temperature of the gas and, by virtue of a higher pressure, by promoting the development of discharge phenomena of greater intensity in parts of the decreasing pressure zone. The gas stream may be heated outside the discharge vessel or heat may be transferred to the gas as it passes through the nozzle. Another important factor is the nature of the gas that is employed since some gases favor the production of discharge phenomena in the decreasing pressure zone and these may then conveniently be admixed as carrier gases to any gaseous reagent that was itself more difficult to excite. The carrier gas might then be injected through the nozzle together with the gaseous reagent. It will also be clear that many of the reactions that occur in the high-energy zone of the discharge, once they have been initiated, will modify the pressure distribution in the decreasing pressure zone and the tendency of discharge phenomena to prefer one part of the zone over another. This may be due to rises in temperature, the evolution of gas, and the like. Moreover, by taking electrical measures such as the superposition of pulses, low or high-frequency alternating currents, the creation of spark discharges, or of additional streams of ions or electrons, conditions may be established in the decreasing pressure zone which will favor the migration of the discharge. In principle any measures will serve this purpose, if they bring about reduction in the resistance to the discharge in the relative part of the zone.

1. In a method of performing metallurgical, chemical or other technical processes under the influence of an electric glow discharge in a discharge vessel containing electrodes which carry an electric potential and provided with insulated leads for applying the potentials to the said electrodes, the steps which comprise charging a gas into the discharge vessel in the region of a first electrode and simultaneously withdrawing gas from the chamber at a point removed from the charging region and at such rates that a pressure gradient is created in the space surrounding the electrode in which the gas pressure diminishes with increasing distance from the electrode, and disposing a cooperating electrode at a distance from the first electrode and in the direction of diminishing pressure, whereby migration of the discharge away from the first electrode and into the zone of decreasing pressure is favored, and the first electrode is at least partly relieved of the load otherwise imposed thereon by the energy of the discharge.

2. A method as claimed in claim 1, wherein the gas is injected through a nozzle and wherein the nozzle is connected as an electrode for creating the electric field, and cooling at least the discharge orifice of the nozzle, whereby the energy density on the surface of the nozzle itself is reduced in favor of the gas-filled space in front of the nozzle.

3. A method as claimed in claim 1, wherein the migration of the discharge is promoted by reducing the resistance to the discharge in part of the decreasing pressure zone.

4. A method as claimed in claim 3, wherein the gas stream is additionally heated.

5. A method as claimed in claim 1, including the step of adding to the gas stream at least one gas which assists in producing a displacement of the discharge.

6. A method as claimed in claim 1, wherein the migration of the discharge is promoted by reducing the resistance to the discharge in part of the decreasing pressure zone and subjecting at least the said part of the decreasing pressure zone to the influence of an additional electric field.

7. A method as claimed in claim 6, characterized by the superposition of pulsed electric discharges.

8. Apparatus for performing the method claimed in claim 1, comprising a discharge vessel enclosing a discharge space, means for creating a glow discharge in said vessel, at least one nozzle projecting into said space and adapted to project a jet into the space through which the glow discharge passes, said means including a ring-shaped electrode arranged co-axially with the axis of the nozzle, the said ring being insulated from the nozzle and connected with one terminal of a source of potential of which the other terminal is connected with the nozzle, additional ring-shaped electrodes arranged at a distance from the first ring-shaped electrode and likewise disposed co-axially with the axis of the nozzle, the said additional electrodes being insulated from each other; a source of potential associated with said additional electrodes and connected therewith and means for withdrawing gas from said vessel to provide a pressure drop in the glow discharge space.

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